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DESIGN AND DEVELOPMENT OF SILVER-CADMIUM STORAGE BATTERIES

Second Quarterly Report,
(NASA Contract No. NAS-1318)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

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PURPOSE

To improve the power output per unit weight of a power supply for an orbiting vehicle, the development of a sealed silver oxide - cadmium battery has been initiated. This battery development contract specifies the requirement of a basic 5 ampere-hour cell capable of cycling for one year at a cyclic frequency of 100 minutes. In addition to cycling, other testing and support development work must be performed. Basically, the other major phases of work to be performed are:

1. The improvement of seals to eliminate or minimize leakage during cycling and stand.

2. Separation evaluation studies to improve the cyclic life of a sealed silver oxide - cadmium cell.

3. Minimize the magnetic properties of the cell.

4. Establish the dynamic testing levels for the cell design.

5. Improve the power output per unit weight.

6. Determine the operating characteristics and activated stand characteristics of the cell at various temperatures.

7. Perform tests to evaluate the couple for extended overcharge periods and to establish the operating pressure as a function of the overcharge current.

I. INTRODUCTION

During this reporting period, basic experimental studies were completed and cyclic studies initiated. The following is a brief description of these projects:

1. A 10% depth of discharge cycling test, using cylindrical "D" size cells, is being conducted at 80° ± 10° F, and at an absolute pressure of less than 100 microns of mercury absolute.

2. Cylindrical cells were subjected to 20% depth of discharge cycling test. This test was performed using the cylindrical cells at 80° ± 10° F and at atmospheric pressure.

3. The accelerated separation evaluation study, which was initiated during the first reporting period, has been completed.

4. Fabrication of prismatic or rectangular cell was started.

5. Plate efficiencies studied to determine optimum weight ratios and densities to these standards has been initiated.

II. DISCUSSION

A. Cell Materials

The work initiated during this period has been performed almost exclusively with prismatic cells having a rectangular cross section. The cell containers are drawn from Type 321 stainless steel and are available in various sizes from which a cell container has been chosen which is adequate to produce the necessary 5 ampere-hours. The dimensions of the cans are as follows:

Outside Length	1.469 ± .010 inches
Outside Width	0.781 ± .010 inches
Height	4.000 ± .010 inches
Wall Thickness	0.019 ± .003 inches

The container covers are also of Type 321 stainless steel and are 0.031 inch thick.

All cells fabricated to date have contained nickel terminals due to the lead time necessary to have non-magnetic stainless steel terminals machined. However, stainless steel terminals have been promised during January and will be used in all subsequent cell fabrication.

It was stated in the First Quarterly Report that non-magnetic expanded stainless steel grid would be evaluated for possible use in this application. A test sample was obtained, but the excessive cold working of the material during the expanding process had hardened the material to such a degree that it was impossible to use. Attempts at annealing the grid in a standard inert gas furnace improved the handling characteristics of the material, but left a very hard oxide coating that was undesirable. Attempts to remove the oxide coating from the grid were not satisfactory, and none of the commercial special metals companies would guarantee an oxide-free annealed grid. Therefore, investigations into the procurement of other materials were continued.

Two other materials have been found that appear to have merit for this application. A sample of one of these materials was forwarded to NASA for the testing of its magnetic properties. This material, commonly called 18% nickel silver, is really an alloy of nickel, copper and zinc. The other material that might possibly be used is cupronickel. Both of these materials are presently being tested for resistance to oxidation and reduction in vented cells, and some 18% nickel silver is being processed into silver oxide and cadmium plates for use in sealed cells.

The evaluation of various separator materials has produced some very erratic results. Consequently, the test cells that have been fabricated during this reporting period have contained various combinations of separators that have produced good results in vented cell tests. All

test cells contained woven nylon as the inert separator next to the positive (AgO) plate. Various combinations of cellophane and Permion 300 were used as barrier membranes, with a matted nylon material (Pellon 2100) used as the wettable separator next to the negative (Cd) plate.

Other types of membranes have recently become available and will be evaluated for possible use in this system.

During this period of work, seal design has been concentrated on the compression type seal rather than the glass type seal. The compression seal consists of three major components: A teflon inner retainer, an O-ring between the teflon retainer and cell cover and around the positive terminal, and a nylon outer retainer. The teflon inner retainer is constructed to serve a dual purpose, the first being to insulate the positive terminal from the cell container and cover. Secondly, it is constructed to assure that the terminal does not turn which would cause shorting or severing of the tab-to-terminal connection. The O-ring is compressed between the terminal and the cover, thereby affecting a positive seal. This condition is aided by tapering the terminal hole in the cover. The nylon retainer is machined with a compression ring on one side. This ring is essential as it compresses the O-ring from the outer side and it also seals the terminal opening in the cover. Finally, an epoxy compound is applied about the terminal to assure tightness of the seal.

In cell fabrication, this compression seal is very easy to affect, but in some cases, prolonged cycling has produced slight leaks around the teflon O-ring. A subsequent analysis of a leaking cell showed a slight cold flow of the inner retainer and O-ring. To remedy this situation, the cell cover has been redesigned to allow a greater compression of the O-ring, thereby restricting the space available for cold flow. These seals are presently being tested and appear to be dimensionally superior to the original O-ring seals.

The improved seal, as described above, has been leak-tested on a mass spectrometer. The seal was in a cylindrical cell container and its leak rate was determined to be 1.1×10^{-7} cc of helium per second at a 15 psi differential. Since it is not feasible at the present time to leak-test the completed cells with the mass spectrometer, new leak-testing techniques and apparatus will have to be devised to assure proper sealing for every cell.

Inquiries have been made to several of the leading ceramic manufacturers into the possibility of obtaining a reliable, inexpensive ceramic seal. Some samples have been received from the Electronics Materials Corporation of Waltham, Massachusetts, and these samples are presently being tested to determine if they are suitable for sealed cell usage. Should these seals prove satisfactory during this preliminary testing, some seals will be purchased and extensive testing initiated.

Preliminary basic efficiency studies have shown that for normal temperature usage (80 ± 10° F), a ratio of negative to positive

weight of 1.33 to 1.00 is preferable. All test cells fabricated during this reporting period were based on this active material ratio. However, further testing indicates that this ratio can be decreased and the cell balance maintained by regulating the original state of charge of the plates. All test cells fabricated during this quarter utilized the 1.33 to 1.00 ratio of plate weights.

B. Cell Fabrication

In the fabrication of the rectangular cells, seven positive and eight negative plates are used, the sizes of which are 1.25 by 3.00 inches. The tab-to-plate connection, in all cells fabricated thus far, has been made by spotwelding the tab to the grid of the fully formed plate. This type of connection has been found to be marginal from a standpoint of strength and consequently, future cells will have tabs attached to the grid before the active material is applied to the grid. These tabs are of 0.005 inch stainless steel material.

To separate the plates, two positive plates are laid end to end and wrapped with one layer of #9526 nylon nearest the plates, and three layers of barrier separator. The separated plates are folded together and a negative plate, which has one layer of Pellon around it, is inserted between them. This method of separating plates minimizes internal shorting of the cell due to "sloughing" of active material and should add to the cycle life of the cell. These separated plates are then combined to form a cell core consisting of seven positive and eight negative plates.

After the cell core has been separated, the positive and negative tabs are crimped and spotwelded to form a single positive and single negative tab for attachment to their respective terminals. These tabs are then cut to length and inserted in the spade portions of their respective terminals. The spades are then crimped and spotwelded to complete the terminal connections.

Since the negative terminal is silver soldered to the cover prior to the tab-to-terminal connection, the seal as previously described is not required for the negative terminal. The inner portion of the seal is attached to the cell core and the core is then placed in a cell container and the cover heliarc-welded to the container.

Before the outer portion of the seal is applied, the cell is activated with 1.303 specific gravity potassium hydroxide through the positive terminal hole. After activation, the final seal at the positive terminal is made and the cell is then completed.

All materials used for present cell fabrication, with the exception of the terminals and grids, are non-magnetic. During the next quarter, these components should be available in quantity to allow the fabrication of a totally non-magnetic cell.

C. Rectangular Cells vs. Cylindrical Cells

The separated core of the rectangular cell lends itself more readily to final inspection than does the cylindrical cell core. Also, the method of separation of the rectangular cell protects more efficiently against internal shorting. It is also felt that the rectangular cell lends itself more readily to controlled mass production.

On the other hand, power output of the rectangular cell is not as great as that of a cylindrical cell of comparable volume in small sized cells. Because of the space required for the inner retainer, terminal spades and tabs, full utilization of the rectangular container volume is not possible. This space amounts to about 25% of the total volume. In the cylindrical container, nearly full utilization of the volume is possible with more than 90% of its volume being available for use. The power output of the nominal 5 ampere-hour cylindrical cell is approximately 1.75 watt-hours per cubic inch, while for the similarly rated rectangular cell, the power output is 1.65 watt-hours per cubic inch.

D. Cell Testing

1. Ten Percent Depth of Discharge Test

During this reporting period, eighteen cylindrical "D" cells were fabricated for specific cyling tests. The original capacity test performed on these cells showed that the average cell capacity was 5.1 ampere-hours. This capacity indicated that the discharge efficiency of the cells was not as high as was desired, but would still be high enough for cyclic testing.

Ten (10) cells were connected in series for testing to a 10% depth of discharge at a 100-minute cycling frequency. The battery was placed in a chamber and the chamber connected to a mechanical vacuum pump. The absolute pressure inside the chamber is maintained at less than 100 microns. The battery discharges through a fixed resistance for 40 ± .5 minutes and is charged, using a modified constant voltage charger (Harrison Laboratories #855 B) for 60 ± .5 minutes. A measure of the input and output were recorded during the first two cycles. The output was 0.55 ampere-hour and the input was 0.56 ampere-hour. This represents a depth of discharge of 11%. The end of charge and end of discharge voltage for each cell is recorded once each day. Figure No. 12 shows the test in operation and the various required equipment. The charge voltage is set at 1.65 volts per cell with the charge current limited to 1.93 amperes. The end of discharge voltages have been very consistent, while the end charge voltages have varied tremendously. Table No. VII shows the end of charge voltage of all the cells at various cycles. The table shows that the charge voltage of some of the cells has remained consistently high throughout the entire test, while others have varied. The reason for this great variation is not clear and therefore, no comprehensive explanation is offered at this time.

This ten-cell battery completed 527 cycles under perfectly normal conditions. During the 527th cycle, an extremely low discharge voltage was recorded for Cell No. 13. The test was temporarily stopped while the cell was removed from the circuit. The resistance was readjusted and the cycling continued on the nine-cell battery. For orbital use, this cell failure would have constituted a battery failure, but for practical testing, it does not justly evaluate the system. The nine-cell battery has completed over 1000 cycles with no indication of further cell failure.

A "post mortem" of Cell No. 13 showed that the failure was mechanical. The current carrying connector had broken loose at the positive plate, thus producing a high resistance current path from the plate to the terminal.

Figure No. 13 is a graph of the discharge voltage of the original ten-cell battery, and also the present nine-cell unit. The two very significant items shown on this graph are the decay of the divalent oxide voltage level over extended cycles, and the stability of the monovalent oxide voltage level. The reason for the loss of the divalent oxide voltage is not clearly understood at this time. However, in a vented cell this divalent voltage can be recovered by extended overcharging of the cell for five or six cycles. In a sealed cell, the overcharge rate sufficient to produce this effect cannot be attained without reaching prohibitively high pressures. Tests are presently being performed to give a more thorough basic understanding of positive plate charging characteristics and to try to isolate the factors contributing to this voltage loss.

In November, a test was initiated at normal atmospheric pressure and 80° ± 10° F, with a battery containing eight cells. As in the other test, the Harrison Laboratories charger was used during the charge portion of the cycle, controlling the voltage at 1.65 volts per cell and 1.93 amperes maximum. Also, a resistive load was applied during discharge, with the depth of discharge being 20%, or 1.0 ampere-hour. Again, a cyclic frequency of 100 minutes was used, consisting of 40 minutes discharge and 60 minutes charge time. A Rustrak recording ammeter and recording voltmeter were used to record battery voltage and current.

The battery completed 510 cycles before any cell voltage of less than 1.0 volt was noted. After this period of cycle, two cells displayed lower cell voltages. These cells were observed closely during the next charge and discharge cycle, and the end-of-discharge voltage had decreased to an even lower level. At this time, the test was terminated. The remaining cells were charged for 16 hours on a Harrison Laboratories Charger #855 B, and then discharged at a 2-ampere rate to determine the remaining capacity. Table No. VIII shows the cell capacities obtained from this test. Subsequently, a "post mortem" on both Cell Nos. 18 and 20 showed that a small short had occurred at the point where the current-carrying tab had been spotwelded to the positive plate. Since this appeared to be a re-occurring fault with the cylindrical cell design, a new method of making this connection was devised and is presently being tested.

The accelerated separation evaluation test, which was discussed in the previous report, was completed during this reporting period.

This test consisted of eight cells flooded with electrolyte and utilizing various separator combinations. The separators used in the construction of these cells were as follows:

Cell No.	Wraps about Positive	Wraps about Negative
1	1 #9526 Nylon, 1 #133 Visking	1 #R-75-D Viskon
2	1 #9526 Nylon, 2 #133 Visking	1 #R-75-D Viskon
3	1 #9526 Nylon, 2 #600 Cello.	1 #R-75-D Viskon
4	1 #600 Permion, 2 #300 Cello.	1 #R-75-D Viskon
5	1 #9526 Nylon, 1 #133 Visking	1 #R-75-D Viskon
6	1 #9526 Nylon, 3 #600 Cello.	1 #R-75-D Viskon
7	1 #9526 Nylon, 3 #300 Cello.	1 #R-75-D Viskon
8	1 #9526 Nylon, 1 #300 Permion, 1 #133 Visking	1 #R-75-D Viskon

These cells were then placed on automatic cycling which consisted of 20 minutes discharge time and 40 minutes charge. During the discharge portion of the cycle, 20 ampere-minutes were removed from the cells, and 34 ampere-minutes were replaced during charge. This amounted to 70% overcharge in each cycle.

Cell No. 2 failed after 949 cycles, and a "post mortem" of the cell revealed no visible shorts. Failure of the cell was contributed to the badly oxidized state of the separator. After 1768 cycles, they were placed on open circuit voltage stand for nine days. A check of the voltages of the cell after the stand period showed that Cell Nos. 4, 6 and 8 still had an open circuit voltage of 1.42 volts. The open circuit voltage of the other cells had decayed to a maximum of 1.18 volts, thus indicating that shorting of various degrees had occurred.

From this basic study, it was decided to use the separator materials as previously described in future cell fabrication. Also, new separator materials have been obtained and similar evaluation tests will be initiated to determine their value for extended cycle life.

Due to a shortage of rectangular containers, no cyclic studies of the rectangular cell have been initiated as yet. Before the next reporting period, three cyclic tests will be initiated to determine the operating characteristics of these cells at various temperatures. However, many spot tests have been performed on the rectangular cells that were fabricated for construction evaluation. These spot tests include manually controlled discharges to an end voltage of 0.9 volt per cell. During these deep discharges, a significant decrease in capacity has been noted. This decrease occurs immediately and continues until nearly 30% of the original capacity has been lost. This significant loss is

being investigated under a basic cell study for the U. S. Army Signal Research and Development Laboratories, and progress will be reported during the next quarterly report on their Contract No. DA-36-039-sc-85370. However, it is felt that the present rectangular design can be constructed to provide capacity in excess of 5 ampere-hours and long cycle life, even with this capacity loss. This is due to the fact that the nominal capacity of this cell is in excess of 9 ampere-hours, while being used for a 5 ampere-hour application. Should a solution to the capacity loss problem be found, the cell could then be considerably upgraded.

Figure No. 14 is a graph of ampere-hours versus cycles for the initial eighteen cycles of discharge on six rectangular cells. Each cell was discharged to an end voltage of 0.90 volts per cell and the average capacity plotted to produce the curve. This immediate capacity loss can be contributed in part to the loss of active silver from the positive plate to the adjacent separation, and also to the low on-charge voltage which was restricted to 1.55 volts per cell. It appears that to charge the positive plate to a degree that will allow high output, an on-charge voltage in excess of 1.80 volts per cell is required. Since at this voltage the charge efficiency is very low and free oxygen is being liberated, an extremely high pressure would have to be contained to produce this effect. However, the cell capacity will level off at approximately the six (6) ampere-hour level and should decrease only slightly on subsequent cycling.

III. PROGRAM OF WORK FOR THE THIRD QUARTER

The following is a list of investigations to be made during the third quarter of this contract:

1. Finalize and test the design of a practical seal to minimize or eliminate cell leakage during battery operation.

2. Fabricate three, ten-cell batteries of rectangular configuration, to be utilized for cyclic studies at controlled temperatures of 20°, 80° and 120° F. These cells will contain all non-magnetic materials, with the exception of the grid, which has not as yet been approved by NASA.

3. Investigate and improve rectangular cell design to obtain maximum utilization of cell void, thereby increasing power output per unit weight.

4. Fabricate rectangular cells, using non-magnetic materials as previously stated, in an effort to finalize cell design.

5. Continue investigations of various methods of balancing cells for battery operation.

6. Initiate further separation studies for the evaluation of new separator materials.

IV. DISTRIBUTION OF ENGINEERING HOURS AND MATERIALS

The following is a list of engineering personnel and technicians associated with this contract, the hours of work performed by each, and the cost of materials purchased during the second reporting period:

NAME	TITLE	HOURS
Morse, E.	Senior Engineering Supervisor	75
Sieglinger, F.	Project Engineer	259
Dittman, F.	Battery Engineer	243
Call, D.	Battery Engineer	382
George, J.	Battery Engineer	126
Carr, D.	Technician	527
Cook, A.	Technician	496
	TOTAL	2,108

Purchased Material Costs . . . . . $ 6,331.55

APPENDIX

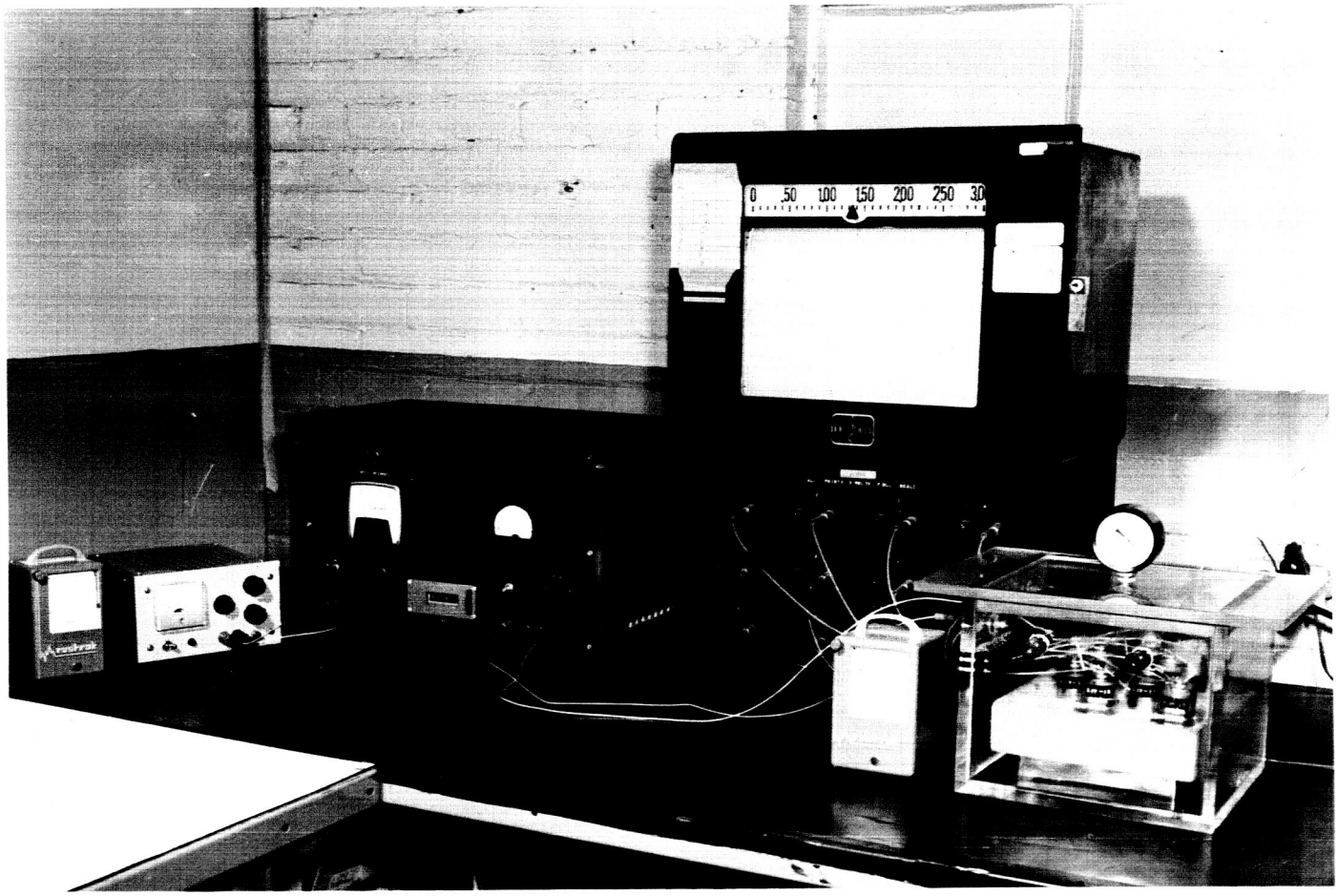

FIGURE 12

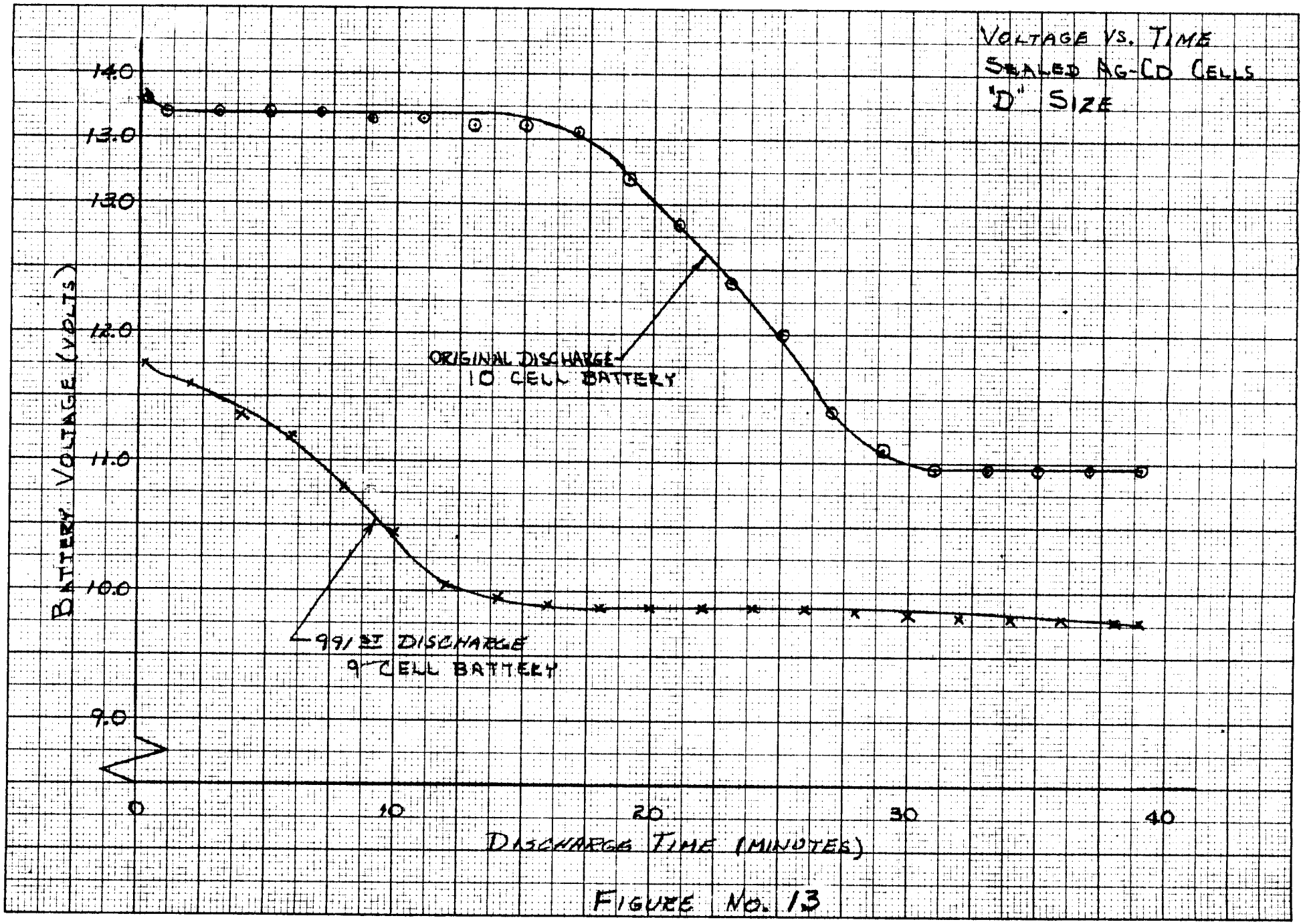

FIGURE NO. 13

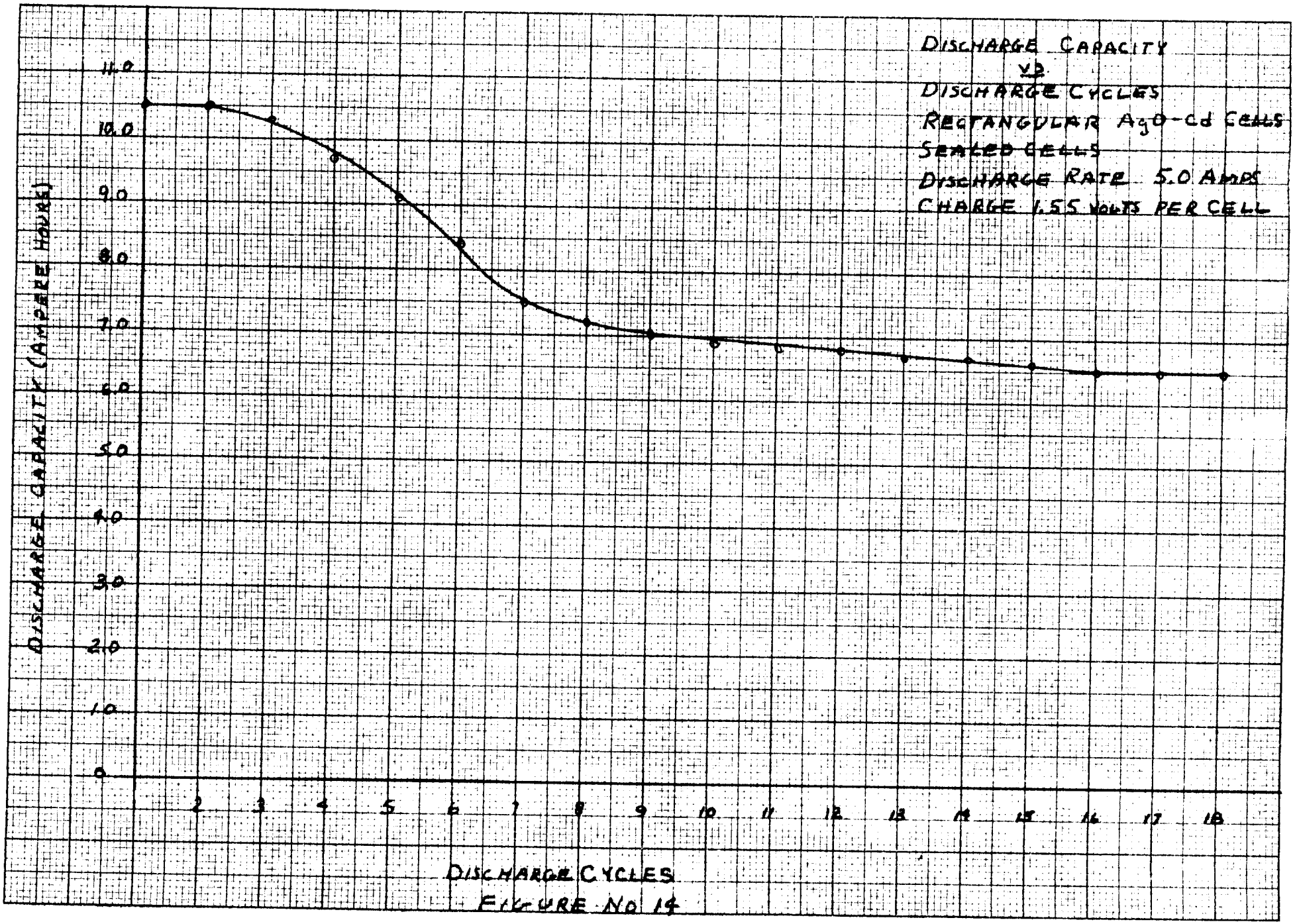

FIGURE NO 14

TABLE NO. VII

END-OF-CHARGE CELL VOLTAGE

CYCLE NO.	3	4	6	7	8	11	12	13	16	19
14	1.72	1.71	1.70	1.45	1.46	1.65	1.72	1.46	1.69	1.50
97	1.44	1.68	1.43	1.44	1.56	1.70	1.72	1.54	1.71	1.67
198	1.43	1.76	1.43	1.43	1.43	1.79	1.80	1.42	1.78	1.68
299	1.45	1.45	1.43	1.42	1.41	1.43	1.82	1.82	1.84	1.79
401	1.42	1.43	1.85	1.43	1.42	1.43	1.80	1.60	1.81	1.71
502	1.43	1.84	1.43	1.43	1.43	1.84	1.44	1.43	1.85	1.81
601	1.85	1.43	1.85	1.43	1.43	1.43	1.82	*	1.82	1.80
702	1.44	1.84	1.44	1.43	1.44	1.86	1.82		1.82	1.80
803	1.85	1.44	1.44	1.43	1.43	1.82	1.82		1.83	1.82
904	1.86	1.43	1.43	1.42	1.42	1.83	1.84		1.83	1.81

* Cell No. 13 removed from test after 527 cycles.

TABLE NO. VIII

CELL NUMBER	FULL CAPACITY AFTER 511 CYCLES -Ampere Hours-
1	2.4
2	2.4
9	1.9
14	2.8
15	1.6
17	2.7
18	1.1
20	1.0